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J. G. Tobin, S. W. Yu, B. W. Chung, G. D.  
Waddill, J. D. Denlinger

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# Direct Comparison of the X-ray Emission and Absorption of Cerium Oxide<sup>a</sup>

J.G. Tobin<sup>1,b,c</sup>, S.W. Yu<sup>1</sup>, B.W. Chung<sup>1</sup>, G.D. Waddill<sup>2</sup>, and J. D. Denlinger<sup>3</sup>

1. Lawrence Livermore National Laboratory, Livermore, CA
2. Missouri University of Science and Technology, Rolla, MO
3. Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, CA

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b)American Vacuum Society member

c)Corresponding Author, [Tobin1@LLNL.Gov](mailto:Tobin1@LLNL.Gov)

## Abstract

X-ray Emission Spectroscopy (XES) and X-ray Absorption Spectroscopy (XAS), have been used to investigate the photon emission and absorption associated with the Ce3d<sub>5/2</sub> and Ce3d<sub>3/2</sub> core-levels in CeOxide. A comparison of the two processes and their spectra will be made.

**Materials terms:** Cerium, Oxygen, X-ray Absorption Spectroscopy, X-ray Emission Spectroscopy

## I Introduction

Recently, we reported the observation of a very strong resonant effect in the Resonant Inverse Photoelectron Spectroscopy of CeOxide. [1] It has now become apparent that there is a utility in a direct comparison of the X-ray Emission Spectroscopy (XES) and X-ray Absorption Spectroscopy (XAS) of similarly prepared CeOxide samples. That comparison is made in this Brief Report/Comment.

## II Experimental

The XES experiments were carried out onsite at Lawrence Livermore National Laboratory, using a spectrometer [2] with capabilities for performing both spin resolved Fano spectroscopy [3] and high energy Inverse Photoelectron Spectroscopy (IPES) or

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Bremstrahlung Isochromat Spectroscopy (BIS). [4] The XES spectra were collected using a Specs electron gun for the excitation and the XES 350 grating monochromator and channel plate system from Scienta as the photon detection. Spectra were collected in “normal mode,” where the electron gun kinetic energy (KE) and the energy position of the center of the channel plate were both fixed and the energy distribution in the photon (h $\nu$ ) spectrum was derived from the intensities distributed across the channel plate detector in the energy dispersal direction. The polycrystalline Ce sample was oxidized by exposure to air at ambient pressures. After introduction to the ultra-high vacuum system, the oxidized sample was bombarded with Ar, to clean the topmost surface region and stabilize the surface and near surface regions. Although CeO<sub>2</sub> would be the thermodynamically preferred composition in an oxygen rich environment, the combination of a vacuum environment and ion etching may have driven the near surface region into a Ce<sub>2</sub>O<sub>3</sub> stoichiometry. [5] XES data collection occurred with the sample at or near room temperature. The base pressure of the system was  $3 \times 10^{-10}$  torr, but the pressure changed depending the energy and current of the electron gun. For example, with the XES measurements at KE = 3KeV, the pressure was approximately 8 to  $9 \times 10^{-10}$  torr and the excitation current to the sample was typically 0.01 mA. More detail of the sample preparation and analysis can be found in Reference 1. The XAS experiments were performed at Beamline 8 of the Advance Light Source, as part of a larger collaboration. [6,7] The ex situ sample used at the ALS was prepared in a fashion similar that that described above.

## **III Spectral Results, Discussion and Conclusions**

A schematic of the XAS and XES processes is shown in Figure 1. To a certain extent, XAS and XES are reversed events relative to each other. However, XAS involves the

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absorption of an x-ray and the movement of an electron into the unoccupied states, i.e. the Conduction Bands (CB), leaving a hole in the core level. In XES, the core hole is induced by electron bombardment and a photon is ejected in the decay process, with an electron moving from the occupied states, i.e. the Valence Bands (VB), into the core hole. The decay-process can be complicated by alternate decay-routes, as illustrated in the right-most panel. While the dominant energy contribution is the binding energy of the core level, there are also small adjustments ( $\Delta$ ) associated with either the CB or VB. The net effect of this is to shift the XES features to lower photon energies than the corresponding XAS features. More discussion and description of the XES and XAS processes can be found in References 1 and 6.

An example of our XES data can be seen in Figure 2. Here, there are two main peaks at  $h\nu = 880$  eV and  $h\nu = 898$  eV, corresponding to the  $\text{Ce}3d_{5/2}$  and  $\text{Ce}3d_{3/2}$ , respectively. The  $\text{Ce}3d_{5/2}$  exhibits substructure, associated with contributions from the underlying Ce metal and near surface CeOxide. This will be discussed more below.

The XAS results are shown in Figure 3. Our results, using a Ce sample oxidized ex situ, are shown in the middle pair and upper pair of curves. A pair of reference spectra, provided by J. Denlinger, is bottom-most. The pairs correspond to data collected using total electron yield [6] and total fluorescence yield. [10] In many respects, there is not much new here. The topmost pair and bottom-most pair, particularly the total electron yield data, reproduce results reported earlier by Kaindl et al. [8], for metallic Ce and  $\text{CeO}_2$ , respectively. The topmost spectra are also essentially identical with our XAS data from a pristine evaporated Ce film, collected on neighboring Beam-line 7 at the ALS. [6] Interestingly, the data in the topmost pair was collected after scraping in vacuum the Ce sample that had been

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oxidized ex situ. Hence, surprisingly good XAS results for metallic Ce were obtained here by preparing an ex situ oxidized sample and then scraping it in vacuum. Moreover, the middle pair of spectra, from the unscraped sample and including the effects of near surface oxidation, will be representative of the results a sample preparation process very similar to that used in the XES experiments. From the above, one can conclude that the higher photon energy features in the  $3d_{5/2}$  manifold arise from the oxide, while the lower photon energy features correspond to the Ce metal. This assignment is confirmed when compared to the results from the reference CeOxide film, the bottom-most pair in Figure 3. Before going on to the comparison of the XES and XAS, it should be noted that the  $Ce3d_{5/2}$  and  $Ce3d_{3/2}$  XAS peaks are of approximately the same intensity. This observation is approximately consistent with the assumption of statisticality, where intensity scales with the number of core states: here 6:4 for  $Ce3d_{5/2}:Ce3d_{3/2}$ .

A visual comparison of the XES and XAS results in Figures 2 and 3 confirms the assignments to Ce metal and CeOxide, as shown in Figure 2 and discussed in Reference 1. Additionally, it is clear that the XES intensities are non-statistical, probably driven by the presence of alternate decay routes as illustrated in the right-most panel in Figure 1. Lastly, the expectation that the XES will occur at slightly lower photon energies, relative to XAS, is also confirmed.

## **Acknowledgements**

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K.T. Moore prepared the ex situ sample and aided in the data collection in the ALS experiments. The synchrotron radiation experiments were carried out at Beamline 8 at the Advanced Light Source at Lawrence Berkeley National Laboratory, Berkeley, CA, USA.

The ALS was constructed and is operated with support from Office of Basic Energy Science in the Department of Energy. We would like to thank the staff of the ALS for their support.

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## Figure captions

- Figure 1      Energy level diagrams for XES and XAS. See text for details.
- Figure 2      XES results for an electron excitation kinetic energy (KE) of 3KeV and monochromator slits of 20 micrometers for the detector. See text for details.
- Figure 3      XAS results from the ALS. See text for details.

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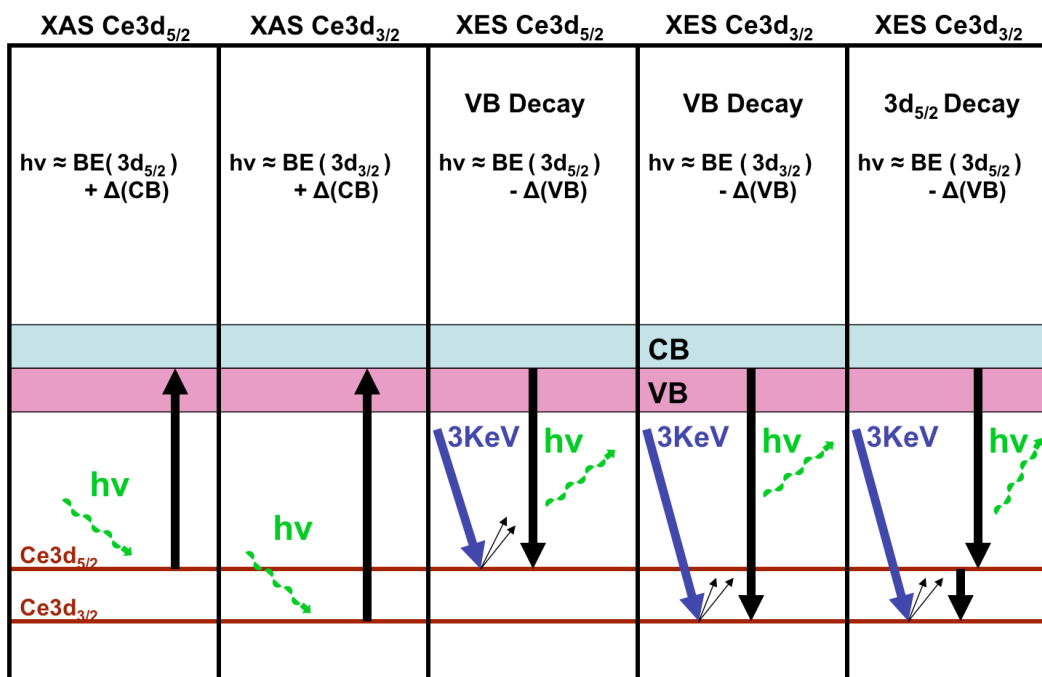


Figure 1



# Direct Comparison of the X-ray Emission and Absorption of Cerium Oxide<sup>a</sup>

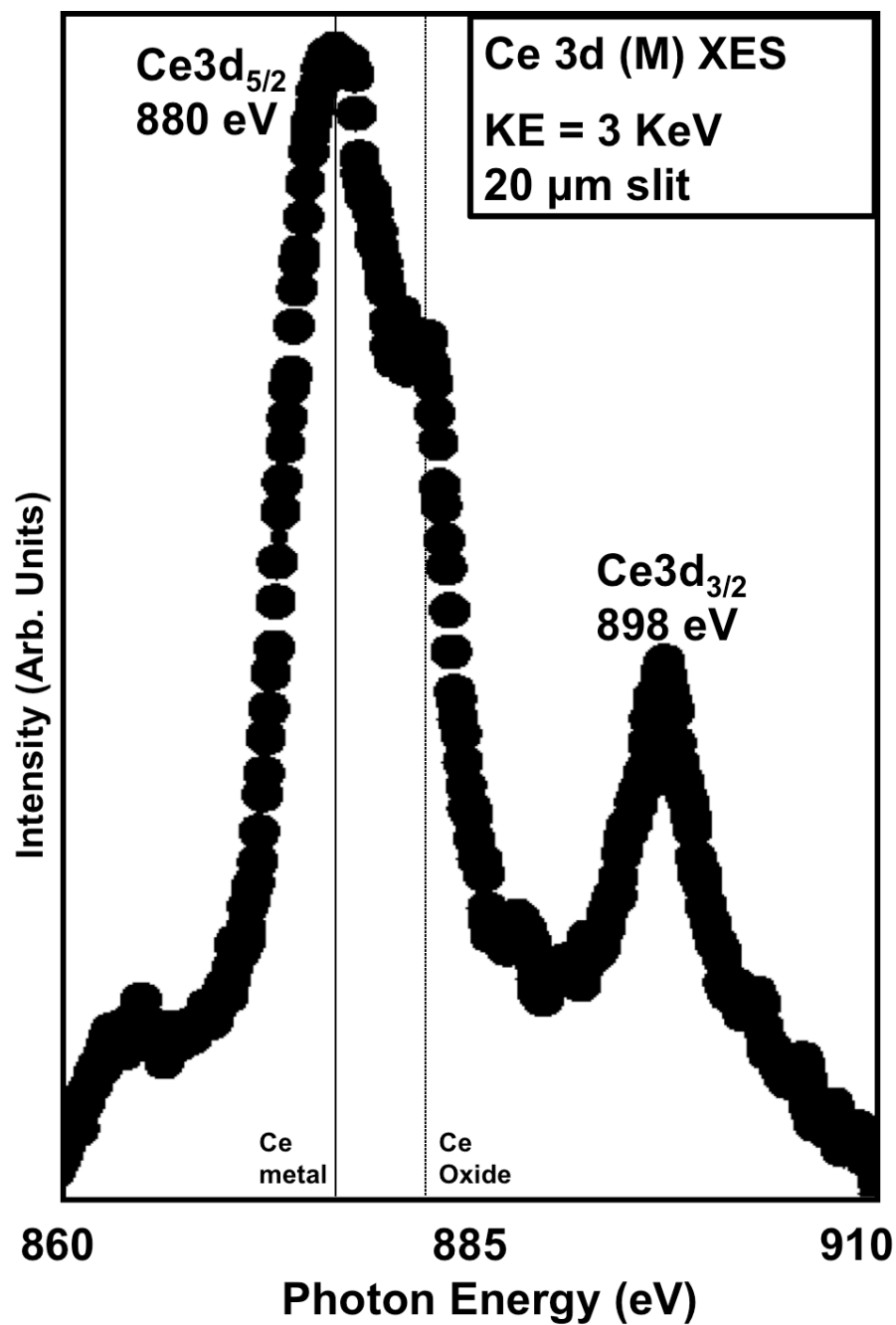


Figure 2

# Direct Comparison of the X-ray Emission and Absorption of Cerium Oxide<sup>a</sup>

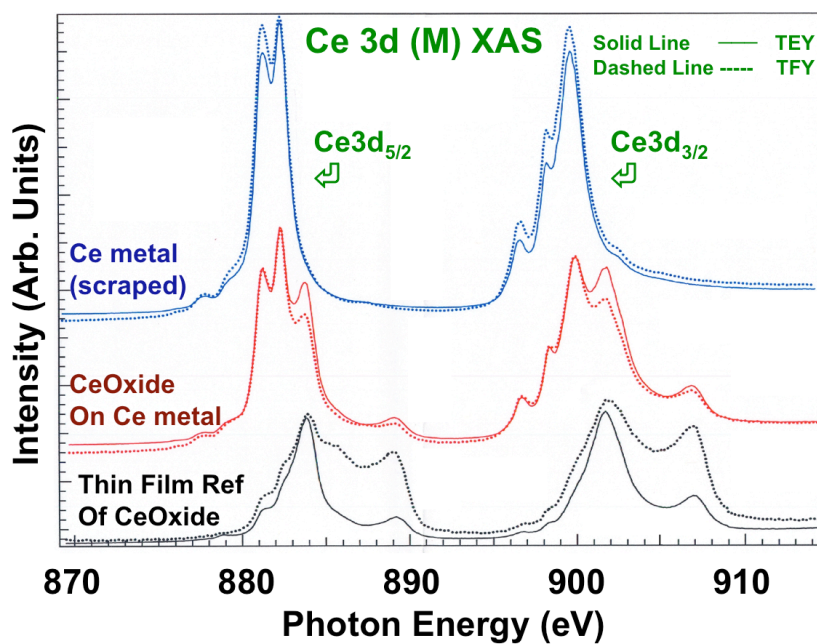


Figure 3